Glass and Ceramics, Vol. 70, Nos. 5 – 6, September, 2013 (Russian Original, Nos. 5 – 6, May – June, 2013)

UDC 620.1:691.3:661.683

PROCESS PARAMETER OPTIMIZATION FOR SYNTHESIS OF HIGH-SILICA LIQUID-GLASS COMPOSITES FOR CONSTRUCTION

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Translated from *Steklo i Keramika*, No. 5, pp. 11 – 17, May, 2013.

The technological factors intensifying hardening and structure-formation in the system quartz-sand – liquid-glass are studied. The temperature-moisture conditions for the solidification of compositions, filler dispersity, modifier form and amount and quantitative ratio of the components of the raw materials mix are optimized. High-silica liquid-glass construction-grade composites with high mechanical strength and water-resistance are worked out.

Key words: high-silica composite, liquid glass, no-roasting technology, strength, water resistance.

The determining factor in the development of most industries, including construction, nowadays is the development of resource- and energy-efficient technologies and their adoption in industry. From this standpoint liquid-glass composites based on abundant raw materials obtainable without high-temperature processing are of great interest for the construction industry.

Liquid-glass composites are synthesized using different minerals fillers, including quartz sand [1 – 6]. Usually, the binder is liquid glass, which because of its high chemical affinity to quartz sand manifests enhanced adhesion properties in compositions. The main advantages of this class of materials are: practicability and versatility (possibility of obtaining articles with a complex shape, coloring, glazing, machining and change of surface relief), minimal energy consumption, extensive raw materials base and environmentally friendly and biologically stable articles. However, most high-silica liquid-glass materials which have been developed do not meet the growing strength and water-resistance requirements in the construction industry (the ultimate compression strength does not exceed 25 – 50 MPa). For composites, high-temperature treatment of molded articles (to 600 – 1000°C) is often used to enhance these properties, but this increases the production costs of the finished products considerably. In this connection the study and optimization of other technological factors that can intensify solidification and structure formation in the system quartz-sand – liquid glass and the development on this basis of materials with enhanced mechanical strength and water-resistance merits attention.

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In the present work high-silica composites were synthesized on the basis of local quartz sand from northern Russia and liquid sodium glass (GOST 13078–81) (Table 1) using the following technological scheme:

– sieving and comminution of quartz sand;

– mixing of quartz sand with liquid glass to obtain a uniform raw material mixture;

– formation of blanks;

– low-temperature processing.

The conditions for forming blanks from a prepared raw materials mixture must permit shape formation of an article with a prescribed configuration without separation, cracking and destruction of the blank's geometry. Different molding methods were tested in the present work: vibratory casting, vibratory compaction and semidry pressing. The best results were obtained using semidry pressing with pressure 100 MPa.

TABLE 1. Characteristics of Quartz Sand and Liquid Glass

Indicator	Quartz sand (GOST 8736–93)	Liquid sodium glass (GOST 13078–81)
Chemical composition, %*	96.1SiO_2; 2.02Al_2O_3; 1.01K_2O; 0.26Fe_2O_3; 0.23TiO_2; 0.21CaO	72.57SiO_2; 26.04Na_2O; 0.64(Al_2O_3+Fe_2O_3); 0.43CaO; 0.32SO_3
Size modulus M_s	0.96	–
Silicate modulus M	–	2.86
Density, kg/m^3:		
true ρ_{true}	2650	1460
bulk ρ_{bulk}	1390	–
Void content $V_{m.s}$, %	47.5	–

* Content, wt.%.

Compared with vibratory casting and vibratory compaction semidry pressing makes it possible to reduce filler consumption, avoid separation of the mixture and attain very low porosity in the blank.

Optimization of the process parameters for the solidification of molded articles opens up wide prospects for increasing the operating characteristics of a material. The transformation of a high-silica liquid-glass green compact into a strong silicate stone occurs as a result of complex physical-chemical processes occurring during the solidification of the binder and its interaction with the filler [7]. According to its physical-chemical nature the binder (sodium liquid glass) is a colloidal solution of alkaline silicates of the system $Na_2O–SiO_2–H_2O$, whose structural foundation is comprised of low-polymer hydrated silicon-oxygen anions.

The main process in the solidification mechanism for liquid glass and liquid-glass compositions is dehydration of silicon-oxygen anions and their polymerization with the formation of bulk high-polymerized silicon-oxygen structure — silica gel. The insoluble amorphous silica formed possesses a highly extended surface and is chemically active at the moment of precipitation. It coats the surface of the grains of the mineral filler and, adsorbing strongly on it, binds the filler particles into a dense, strong conglomerate. As a result of these processes the composition acquires strength and water-resistance.

In parallel with the coagulation of liquid glass and precipitation of colloidal silica other processes occur in the solidifying system — partial dissolution of the filler grains in an alkaline medium with formation of monomer and low-polymer ions, neutralization of the alkaline component of the system, for example, by carbon dioxide in air. These processes make an additional contribution to the kinetics of solidification of the composition.

The theoretical ideas presented above served as a basis for optimizing the solidification parameters for blanks, affecting the dehydration process and polymerization and structure formation in a composition: temperature-moisture conditions for solidification; dispersity of the filler; introduction of the modifying additives; and, the quantitative ratio of the components of the raw materials mixture.

Solidification Conditions for the Composition. The solidification conditions affect the kinetics of all physical-chemical transformations in the liquid-glass composition. The factors lowering the OH^- concentration stimulate the formation of siloxane bonds Si–O–Si and formation of a high-polymer, water insoluble, three-dimensional silicon network. For this reason materials based on liquid-glass binder acquire strength as a result of dewatering of the system and hardening of the contacts formed on pressing, which is determined by the external condition of solidification.

The starting point for optimizing the conditions for solidification were the results of differential scanning calorimetry (Fig. 1): degradation of the mixture starts at low (room) temperatures; the maximum dewatering of the system occurs a 65 – 85°C and is completed around 150°C. Based on this the

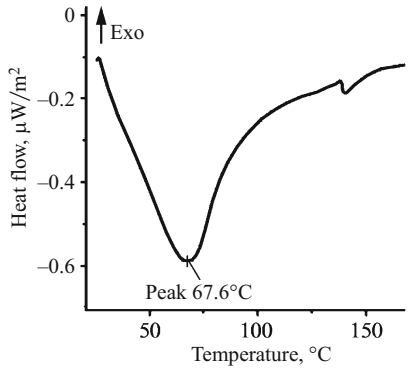

Fig. 1. The results of differential scanning calorimetry of a liquid-glass composition based on quartz sand.

following conditions for the solidification of the blanks were tested: air-dry conditions at room temperature (ADC) for 28 days; drying at 85 – 300°C for 3 h followed by inertial cooling; steam curing (SC) at 85 ± 5°C for 3 h followed by inertial cooling. In addition, the softening ratio K_{soft}, which is used to characterize the water-resistance of construction materials, is calculated as the ratio of the compression strength of samples in the water-saturated state to the strength of the initial dry samples. The physical-mechanical properties of the samples after solidification under different conditions are presented in Table 2.

Steam curing does not give uniform dewatering of a composition with adequate speed and does not lead to the formation of strong material. Air-dry solidification conditions at room temperature promote hardness buildup of the material, but after solidification for 28 days its compression strength does not exceed 30 MPa. The best strength indicators are obtained for samples whose drying time is short. The trend in the variation of the density, porosity and water absorption of the experimental samples as a function of the conditions of solidification correlates with the change in strength — the best values of the properties correspond to the samples which have undergone short-time drying. A drawback common to all synthesized composites is their low water-resistance. Only samples subjected to short-time drying can be referred to as water-resistant, since their softening ratio equals 0.8.

TABLE 2. Results of Physical-Mechanical Tests on Composites after Solidification under Different Conditions

Solidification conditions	Ultimate strength, MPa		Density, kg/m³	Water-absorption, %	Open porosity, %	K_{soft}
	compression	bending				
ADC	30	11	2140	14	25	0.7
Drying	46	18	2040	12	22	0.8
SC	14	7	2050	13	24	0.3

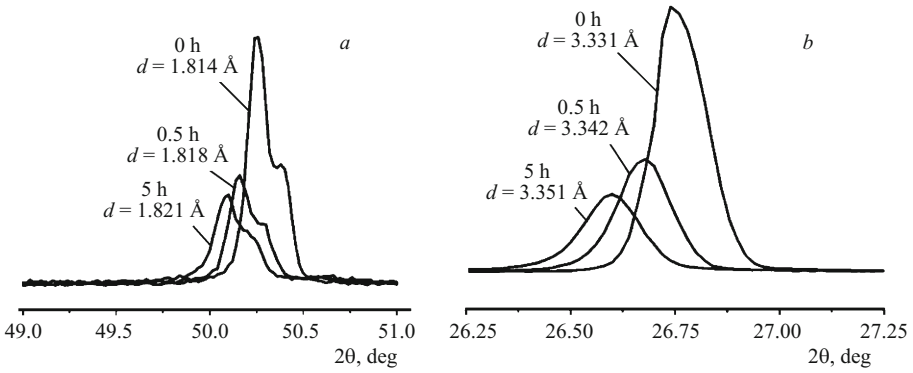

Fig. 2. Main diffraction peaks for quartz in the x-ray diffraction patterns of sand in reflection before (*a*) and after (*b*) comminution.

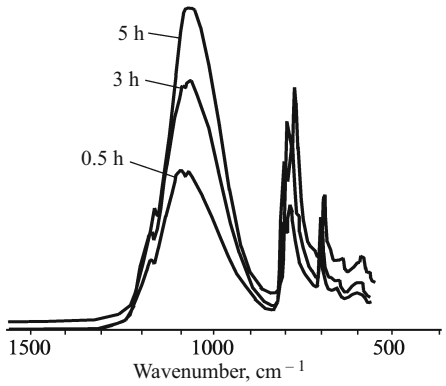

Fig. 3. IR-absorption spectra of sand versus the comminution time (indicated on the curves).

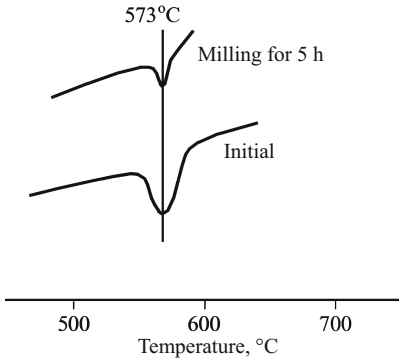

Fig. 4. Endothermal effect corresponding to the polymorphic transformation of crystalline quartz in sand before and after comminution.

In summary, the optimal conditions for dehydration of a composition are created during low-temperature drying of a molded intermediate part. The temperature-time regime of drying includes heating of the blanks to 120°C and isothermal soaking at this temperature for 2 h followed by inertial cooling. Heat-treatment at higher temperatures (to 300°C), which is performed to accelerate the process, results in defective parts because of nonuniform dehydration over the volume. Conversely, a softer drying regime at 85°C with longer soaking time to 6 h promotes the most uniform removal of moisture without cracking of the samples and can be taken as optimal.

Filler Dispersity. Quartz sand used as filler in a liquid-glass composition is chemically inert. For this reason the interaction between the grains of ordinary sand and the liquid glass does not make a large contribution to the strength of the composition. In this case the alkali component is most likely to play the role of an activator of the surface of silica particles and catalyst of polymerization reactions of silica gel.

An effective method of increasing the reactivity of sand is to increase its specific surface area, which is accomplished by fine comminution of the material [8 – 10]. Preliminary experiments established that the largest change in the dispersity during comminution (in a planetary mill) occurs during the initial period of milling — over comminution time 30 min S_{sp} increases 10-fold and equals about 3000 cm^2/g with average particle size 25 μm. For longer comminution times the milling efficiency decreases somewhat.

As for the increase in dispersity, fine comminution of quartz sand destroys its crystalline structure (mechano-activation hypothesis), which should affect the kinetics of the physical-chemical processes accompanying solidification of the raw materials mixture. The structural changes occurring in quartz sand after comminution in the adopted regime are confirmed by x-ray structural analysis, differential scanning calorimetry and IR-spectroscopy. Thus, the general character of the x-ray diffraction diagrams of comminuted sand is preserved, but the fine structure of the main diffraction peaks in reflection of quartz changes — as the milling time increases, the interplanar distances *d* (Å) change and the intensity *I* (counts) of the reflection peaks decreases (Fig. 2). This phenomenon can be interpreted as a decrease in the amount of the crystalline phase in the experimental sample as a result of partial amorphization. The IR-spectra of comminuted sand (Fig. 3) exhibit broadening of the main bands at 1070 – 1030 cm^{-1} and near 770 cm^{-1}, due to vibrations of the bonds Si–O–Si in quartz, which indicates the appearance of silicon-oxygen bonds with a wider set of vibrational characteristics. A comparative analysis of the thermograms of the initial and comminuted sand (Fig. 4) demonstrates a decrease

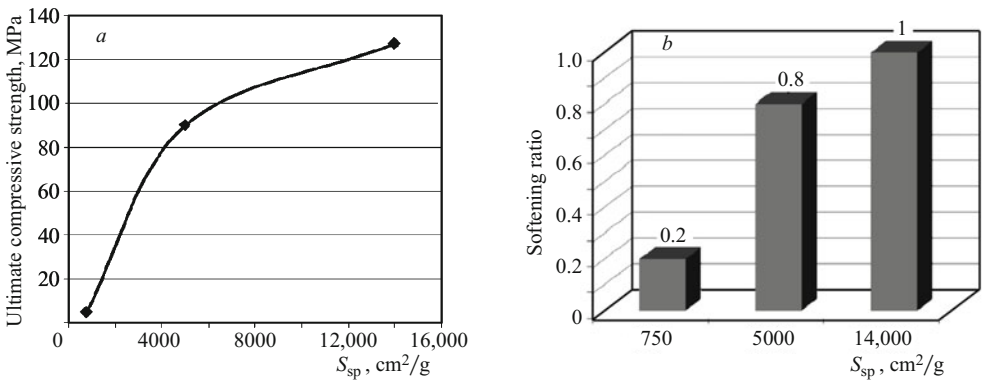

Fig. 5. Effect of the specific surface area of sand on the compression strength (*a*) and the softening ratio K_{soft} (*b*) of a high-silica composite.

in the area of the endothermal effect at 573°C, corresponding to a polymorphic transformation of quartz.

These results make it possible to conclude that even for relatively short milling time the sand undergoes structural changes, manifested as an increase in the defectiveness of its crystal structure and decrease in the amount of crystalline quartz in the samples as a result of the partial amorphization of the grains. The large increase in the active surface of the comminuted sand and the observed changes in the crystalline structure of the grains increase the reactivity of the material.

The use of finely comminuted mechano-activated quartz sand with enhanced reactivity promotes considerable hardening of the high-silica composite owing to the filler-bonder chemical interaction and intensifies the solidification of the composition. The water-resistance of the material also increases. The samples made from sand whose specific surface area is 1.4×10^4 cm^2/g attain compression strength surpassing 120 MPa and exhibit practically no softening in tests for water-resistance (Fig. 5).

In summary, fine milling of sand, which opens up a large active surface and increases the reactivity of sand, activates a chemical interaction of an alkaline solution of sodium silicate with the surface of quartz grains at low temperatures and increases the performance of the material. However, the economic desirability limits ultrafine milling. For this reason, in accordance with the results of an experiment for obtaining no-roasting materials with a liquid-glass binder it is recommended that the dispersity of the filler correspond to specific surface area 5000 cm^2/g.

Modification of the Raw Materials Mix by Ethyl Alcohol. In a number of cases, the use of fine-milled quartz sand in the synthesis of liquid-glass composites causes technological problems in molding the raw materials mixture — clumping of the filler, nonuniform distribution of the binder and sticking of the mixture on the walls of the mold. To prevent these adverse phenomena a raw materials mixture modified by the addition of ethyl alcohol (mixture of tetraethoxysilane $(C_2H_5O)_4Si$ with the products of its partial hydrolysis) was tested. By virtue of its physical properties the modified mixture makes the surface of the sand grains water-repellant and improves the moldability of the mixture. To prepare the raw materials mixture ethyl silicate in amounts 0.5 – 5.0 wt.% was added to the fine-milled sand and the mixture was carefully mixed until a paste with uniform color was obtained. Next, the mixture was mixed with liquid glass and homogenized again. This procedure made it possible to increase the uniformity of the molding paste and prevent it from sticking to the walls of the mold, which greatly decreased the number of defective parts. For high content of ethyl silicate the strength of the material after hardening decreases because a rough hydrophobic film forms on the filler grains, which impedes the interaction between the filler and binder; the content of ethyl silicate in the raw materials mixture should not exceed 3%.

The introduction of ethyl silicate also has a positive effect on the structure of the solidified composite. It is evident in the pre- and post-solidification photomicrographs of the material (Fig. 6) that the molded raw materials mixture comprises a compacted polydisperse mass with no gel-like or

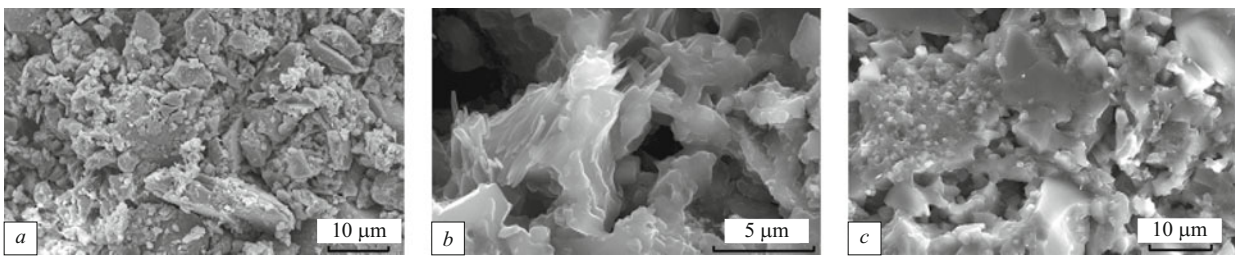

Fig. 6. Pre- and post-solidification microstructure of the samples of high-silica composite: *a*) sample before solidification; *b*) undeformed sample after solidification; *c*) ethyl silicate modified sample after solidification.

TABLE 3. Content (wt.%) of the Components in the Raw Materials Mixtures

Component	Mixture							
	1	2	3	4	5	6	7	8
Sand	74.0	76	76	78	80	80.0	84	84
Liquid glass	25.5	23	19	19	18	19.5	15	13
Ethyl silicate	0.5	1	5	3	2	0.5	1	3

TABLE 4. Properties of High-Silica Composites based on the Mixtures 1 – 8

Indicator	Mixture							
	1	2	3	4	5	6	7	8
Ultimate strength, MPa:								
in compression	97	106	72	111	140	120	80	64
in bending	48	45	–	–	53	40	32	21
K_{soft} (water-resistance)	0.8	1	0.8	0.9	1	1	0.8	0.8

amorphous formations, while in the solidified samples unstructured embryos are clearly seen on the filler grains. The structure of the unmodified sample differs by a nonuniform distribution of the binder because of the aggregation of the highly disperse filler, so that the formation of a new phase does not result in adequate compaction of the material. The modified sample is characterized by a more uniform distribution of the liquid glass, a new phase is observed to form over the entire surface of the filler and in the intergrain space, and the structure differs by high density. This promotes more complete bonding of the sand particles, which has a positive effect on the mechanical properties of the material. In addition, the additional precipitation of silica gel accompanying the interaction of ethyl silicate with liquid glass increases the hydrolytic stability of the finished parts.

Optimization of the Quantitative Ratio of the Components of the Raw Materials Mixture. The strongest contacts in sand-based liquid-glass composites are adhesive contacts between the filler and the silica gel formed during the solidification of the liquid glass, while the cohesive contacts inside the silica gel are much weaker [11]. This makes it necessary to optimize the filler – binder ratio in the composition — the amount of binder must be minimal but adequate for thin adhesive layers to form between the sand grains.

To optimize the composition of the raw material mix a series of materials with variable mass content of the main components was synthesized (sand — 74 – 84; liquid glass — 13 – 25.5; ethyl silicate — 0.5 – 5 (Tables 3 and 4)).

It was determined that increasing the sand content in the raw materials mixture above 80 – 84% decreases the strength characteristics of the material, since a uniform distribution of the binder is not attained between the filler grains. Introducing less than 75 – 76% sand is undesirable, since the thickness of the weakest interlayer of the binding silica gel between the filler grains increases. The best mechanical strength and water-resistance obtain with the following content of the raw materials mixture (wt.%): sand — 80; liquid glass — 18 – 19; ethyl silicate — to 2.

In summary, the creation of favorable conditions for dehydration, polymerization and structure formation in no-roasting high-silica composites based on liquid-glass binder by optimizing the process conditions and production parameters has made it possible to increase the leading performance characteristics significantly — the mechanical strength (σ_c to 140 MPa) and water-resistance (K_{soft} to 1.0).

The work was supported by the Ministry of Education and Science of the Russian Federation under grand 11.G34.310027, GK 16.552.11.7046).

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